

Kinetic and thermodynamic studies of the adsorption of heavy metals on to a new adsorbent: coal mine drainage sludge

Mingcan Cui, Min Jang , Sang-Hyun Cho and Jeehyeong Khim

Introduction

Acid mine drainage (AMD) released from abandoned gold mines can not only pollute natural environments such as surrounding soils, surface and ground waters, but also has some sequential toxic effects on crops and humans through concentration through the food chain [1]. Although the most widespread method to remove heavy metals in AMD is coagulation and flocculation through neutralization by increase of pH, it is not very economic or effective, and can also release secondary pollution. Accordingly, other treatment methods have been extensively studied. Among them, adsorption techniques have been studied, using metal oxide, active carbon, fly ash, peat, activity sludge and waste sludge [2–5]. In particular, research has been conducted on the adsorption of heavy metals by the use of iron compounds including ferric salts and zero valent iron (ZVI) [6,7]. The adsorption of cationic heavy metal species on the hydroxyl group of sorbents has been found to be an endothermic reaction in an adsorption study of heavy metals using goethite (α - FeOOH). Thus, the adsorption capacities and equilibrium constants increase as the temperature increases [8–15]. The relationship between pH and adsorption and/or coprecipitation, using goethite for the removal of heavy metals, has also been actively studied [16]. The different ratios of each hydroxyl group (FeOH_2^+ , FeOH , FeO^-) may depend on the pH. In contrast, clay minerals such as bentonite show a clarification reaction, in which their equilibrium constants and adsorption capacities decrease with an increase in temperature as a result of

the exothermic nature of metal adsorption [17].

In this study, the adsorption characteristics of coal mine drainage sludge (CMDS) for heavy metals in AMD released from a metal-mine area were investigated. The CMDS contains mainly Fe_2O_3 (64.7%) and has been produced by drying the sludge cake produced from an electric purification facility in Korea. The Fe hydroxide/oxide of CMDS is usually amorphous and has amphiphilic adsorption characteristic for both cationic heavy metals and anionic metalloids. Thus, the application of sludge as a sorption material for treating AMD of metal mines could have an economic potential in terms of recycling waste material.

The objective in this study was to investigate the adsorption, in terms of reaction speed and thermodynamics, of the main heavy metals in the AMD released from metal mines – Cu(II) and Zn(II) – on to CMDS.

Experimental

Water and sludge samples

Water was sampled from the effluent of three settling tanks that were previously setup to remediate AMD of a metal mine located at $35^\circ 18' 23.2''$ longitude and $129^\circ 13' 39.1''$ latitude in South Korea. The CMDS was simply prepared by drying at 25°C the sludge taken from an electric purification facility treating acidic mine drainage from a coal mine [18].

Analyses

The surface area of CMDS was analysed by the Brunauer Emmett Teller (BET, ASAP 2010, Micromeritics Inc., USA) adsorption method using nitrogen gas (Sutosorb-1-C, Chemisorptions-Physisorption Analyser, Quantachrome Instruments, USA). The pH of water was measured with a Thermo Orion model 420A+, and

heavy metals were analysed by an inductively coupled plasma atomic emission spectrometer (ICP-AES, 5300DV, Perkin Elmer). X-ray diffraction (XRD, X'pert PRO/MRO, Philips) analyses were conducted for the selected freeze-dried powdered samples of CMDS by use of a PANalytical X'Pert Pro diffractometer (fitted with an X'Celerator) with a $\text{CuK}\alpha$ radiation source at a scan speed of $2.5^\circ \text{ min}^{-1}$.

The phase identification of CMDS was carried out by the means of the X'Pert accompanying software program, High Score Plus, and the reference intensity ratio method (RIR method) ICDD PDF-4+ database (International Centre for Diffraction Database, USA, 1999). The X-ray fluorescence (XRF-1700/SHIM ADZUXRF) results showed that the CMDS was mainly composed of SiO_2 (6.65%), Fe_2O_3 (64.74%) and CaO (8.6%). These compounds exceeded 79.9%.

The buffer capacity of the sludge was measured as follows: 10 g of sludge and 25 mL of deionized water were added to a 50 mL centrifuge tube. Then different amounts of 0.1 M HCl were added to each sample and the suspensions were shaken at room temperature for 24 h prior to pH measurement [2,19]. The sludge was reacted with 2 M HCl to dissolve the carbonate. The remaining acid was titrated using 0.1 M NaOH to measure the CaCO_3 content of the CMDS [19]. The easily extractable fractions of Fe and Mn from the CMDS could be analysed with the following methods. After extraction with 1 M hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$), the Fe content of the CMDS was measured by ICP [20]. The Mn ions in the CMDS were dissolved using 0.1 M hydroxylamine hydrochloride and analysed by ICP [21]. The organic carbon content and cation exchange capacity (CEC) of the CMDS were measured by the Walkley–Black method and the ammonium acetate method, respectively. For the ammonium

acetate method, the CMDS was treated with a salt of NH_4^+ ion and then NH_4^+ ions were substituted using a NaCl solution. The replaced amount of NH_4^+ ions was analysed. Loss-on-ignition (LOI) of the CMDS was measured as follows: 10–20 g of wet CMDS was dried at 105°C for 18 h, and then heated at 450°C for 6 h. During this procedure, the sample at each step was weighed [1].

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